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## DESCRIPTION

METHOD FOR DETERMINING DETERIORATION OF  
CAPACITOR

This application is a U.S. national phase application of PCT  
5 International Application PCT/JP2005/010847.

## TECHNICAL FIELD

The present invention relates to a method for determining the  
deterioration of a capacitor in which electrolytic solution is provided  
between electrode bodies.

## 10 BACKGROUND ART

As a capacitor in which electrolytic solution is provided  
between electrode bodies, an electric double layer capacitor  
(hereinafter also may be simply referred to as capacitor) is known for  
example. The electric double layer capacitor uses a large electric  
15 double layer capacity by a combination of activated carbon that has a  
large specific surface area of electrode material and that is  
electrochemically-inactive and electrolyte. The electric double layer  
capacitor has a characteristic that electrochemical reaction is not  
caused by the charge and discharge and rapid charge and discharge can  
20 be provided with high current, providing a higher power density than  
that of a chemical battery, for example. The electric double layer  
capacitor has been expected for the application to a high-current  
generation circuit, an instant compensation power source, and a load  
leveling circuit for example.

25 When the above capacitor is used for a long time, a dry-up

mode deterioration proceeds in which the inner electrolytic solution gradually evaporates to consequently increase the internal resistance to reduce the capacitance, thus causing the termination of the service life.

One conventional method determines the deterioration of a capacitor by applying a square wave signal having a low frequency as a measurement signal to a target capacitor to integrate a predetermined part of the reply signal to detect the change of the characteristic of the capacitor based on the integration value. This deterioration determination method is disclosed by Japanese Patent Unexamined Publication No. 6-342024. Another conventional method determines the deterioration of a capacitor by controlling the power distribution of the capacitor to determine the deterioration of the capacitor when the inter-terminal voltage of the capacitor reaches a deterioration reference voltage within a predetermined time from the time at which the inter-terminal voltage reaches a predetermined value. This deterioration determination method is disclosed by Japanese Patent Unexamined Publication No. 2001-297954.

Still another conventional method determines the deterioration of a capacitor by measuring the increase of the temperature at the surface of the capacitor. The above-described deterioration determination method is disclosed by Japanese Patent Unexamined Publication No. 2001-85283. A technique regarding an impedance characteristic of a capacitor is disclosed, for example, by "Denki-Kagaku Capacitor, Kiso, Zairyou, Ouyou (which is written by Brian E. Conway and published by NTS Inc. on June 5, 2001, P.393 to P.401).

However, the conventional methods for determining the

deterioration of a capacitor may require a circuit section (e.g., measurement signal source, A/D converter) and a signal processing by CPU, thus increasing the cost of the measurement apparatus and complicating the deterioration detection method. The above  
5 deterioration determination by the temperature at the surface of the capacitor also may cause a problem in the measurement accuracy.

Furthermore, generally-known conventional methods for determining the deterioration of an electrolysis capacitor may cause a huge amount of accumulated measured data. Thus, a circuit  
10 device for determining the deterioration based on the data also may have a high cost and a complicate structure.

Furthermore, when a capacitor in which electrolytic solution is provided between electrode bodies (e.g., electric double layer capacitor) is determined with regards to the deterioration, another  
15 method may be considered by which the capacity component and a DC capacitor resistance (hereinafter referred to as DCR) component are measured and the determination is made based on the measurement result. For the measurement of these capacity component and DCR component, a DC voltage method and an AC  
20 impedance method are known. The DC voltage method measures these capacity component and DCR component based on the behavior of the DC voltage when the capacitor performs charging and discharging. The AC impedance method applies an AC voltage to the capacitor to derive these capacity component and DCR  
25 component from the impedance value.

The DC voltage method provides an accurate measurement result because this method directly measures these capacity

component and DCR component from the DC voltage in the charging and discharging but uses a large amount of charge in the capacitor due to the charging and discharging. Thus, the DC voltage method may cause a situation where much power is consumed for the determination of the deterioration. The AC impedance method consumes less power because this method uses the frequency characteristic of the AC voltage. However, the AC impedance method may cause, when the deterioration of the capacitor is promoted, a value that is smaller than that of the DC voltage method. This may cause a situation where this value is mistakenly determined as representing no deterioration, thus lowering the reliability.

## SUMMARY OF THE INVENTION

The present invention provides a method for determining the deterioration of a capacitor by the AC impedance method having an improved reliability by an increased measurement accuracy.

In the method for determining the deterioration of a capacitor of the present invention, the deterioration of a capacitor including a pair of electrode bodies and electrolytic solution provided between the electrode bodies is determined by applying an AC voltage to the capacitor to measure an impedance characteristic at a frequency of the AC voltage. An inflection point appearing in the impedance characteristic due to the deterioration of the electrolytic solution is previously calculated to compare a characteristic value based on an impedance value in a frequency region lower than the inflection point with a predetermined characteristic value, thereby determining

the deterioration. This method can improve the measurement accuracy in the determination of the deterioration of the capacitor and can suppress power consumed for the determination.

## 5 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a circuit diagram illustrating a method for determining the deterioration of a capacitor according to a first embodiment of the present invention.

Fig. 2 is a cross-sectional view illustrating a method for  
10 determining the deterioration of a capacitor according to the first embodiment of the present invention.

Fig. 3 illustrates an impedance characteristic of the capacitor.

Fig. 4 is a flow diagram of the deterioration determination method.

Fig. 5 is a characteristic diagram illustrating the DCR/Z ratio  
15 of the deterioration limit of the capacitor for explaining the method for determining the deterioration of a capacitor according to a second embodiment of the present invention.

Fig. 6 is a cross-sectional view of an electric double layer  
20 capacitor for explaining the method for determining the deterioration of a capacitor according to the embodiment of the present invention.

### Reference marks in the drawings

1	Electrode body
25 1a	Power collection material
1b	Activated carbon
2	Separator

	3	Electrolytic solution
	4	Housing
	5 and 26	Lead terminal
	6 and 24	Sealing body
5	7, 8, and 11	Characteristic impedance trajectory
	10	Diffusion resistance component
	12, 15, and 16	Inflection point
	13	DCR measurement frequency region
	14	Capacitive frequency region
10	20	Capacitor element
	21	Electrode terminal
	22	Adhesive tape
	23	Metal case
	25	Concave groove
15	27	Grommet fitting
	28 and 52	Electric double layer capacitor
	50	Input power source section
	51	Load section
	53	Deterioration measurement section
20	54	Abnormality display section

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Hereinafter, embodiments of the present invention will be described with reference to the drawings.

25

(First Embodiment)

Fig. 1 is a circuit diagram illustrating a method for

determining the deterioration of a capacitor according to a first embodiment of the present invention. In Fig. 1, input power source section 50 applies a voltage to load section 51 so that load section 51 operates. A part of the voltage charges electric double layer capacitor 52. When input power source section 50 has an abnormality or requires high power, capacitor 52 supplies power to load section 51. Capacitor 52 deteriorates when being used for a long time or being used in some environment. Deterioration measurement section 53 determines the deterioration of capacitor 52 by measuring the deterioration. When the deterioration is determined, abnormality display section 54 reports the deterioration by alarm, display or the like.

Electric double layer capacitors for explaining the method for determining the capacitor deterioration according to embodiments of the present invention have a coin-like shape for memory backup and a cylindrical shape for power. The coin-type electric double layer capacitor (not shown) is provided by sequentially layering a lower discoidal electrode, a separator, and an upper electrode in a short cylindrical metal case in which the upper end is opened to inject electrolytic solution into the case. Gasket for the purpose of insulation and sealing is stored at the inner circumference edge section of the metal case. The upper face of the metal case is covered with a metal cover. The metal case and the metal cover are caulked so that the former does not have a direct contact with the latter.

Fig. 6 shows the structure of a cylindrical electric double layer capacitor for explaining the method for determining the

deterioration of the capacitor according to an embodiment of the present invention. In Fig. 6, electric double layer capacitor 28 has the structure as described below. Power collection material in capacitor element 20 includes long stripe-shaped metal foil, punching metal, expand metal for example. Both faces or one face of this power collection material are/is coated with polarized electrode consisting of activated carbon, carbon, and binder. Two power collection materials coated in the manner as described above are prepared. These power collection materials also have therebetween a long stripe-shaped separator for the purpose of insulation and the retention of electrolytic solution. Each power collection material is connected with one electrode terminal 21. Then, capacitor element 20 is structured by winding the power collection materials in a spiral manner to finally fix the power collection materials by adhesive tape 22. Electrode terminal 21 of capacitor element 20 is connected to grommet fitting 27 provided in sealing body 24. Metal case 23 has a cylindrical shape with a bottom in which the neighborhood of the upper end section has concave groove 25. Lead terminal 26 is outwardly extruded from metal case 23 in which capacitor element 20 is stored. Electrolytic solution (not shown) is injected to metal case 23 and the upper end section of metal case 23 is inwardly bent, thereby sealing metal case 23.

Fig. 2 is a cross-sectional view illustrating another capacitor for explaining the determination of the deterioration of a capacitor in an embodiment of the present invention. This capacitor includes electrode bodies 1 and electrolytic solution 3 provided between



electrode bodies 1. Housing 4 is filled with electrolytic solution 3. Housing 4 includes electrode bodies 1, separator 2 provided between electrode bodies 1, lead terminals 5 respectively connected to electrode bodies 1, and sealing body 6 for sealing housing 4.

5 Electrode body 1 is provided by covering the wall face of power collection material 1a consisting of metal such as aluminum with activated carbon 1b. Separator 2 also may be omitted when electrolytic solution 3 has a high viscosity (e.g., when electrolytic solution 3 has gel-like texture).

10 The determination of the deterioration of a capacitor according to the first embodiment of the present invention is performed by using deterioration measurement section 53 to make the determination by the measurement by the AC impedance method. Although the AC impedance method can provide a measurement  
15 with a significant power saving, it is important to increase the measurement accuracy to improve the credibility of the measurement result.

Fig. 3 illustrates the impedance characteristic of the capacitor according to the first embodiment of the present invention. The  
20 capacitor according to the first embodiment is applied with an AC voltage and the impedance characteristic at the frequency of the AC voltage is measured. In Fig. 3, the vertical axis represents impedance values while the horizontal axis represents frequencies when a fixed AC voltage is applied to the capacitor. Both of the  
25 vertical axis and horizontal axis are logarithmic axes. The impedance characteristic at the initial stage of the use of the capacitor according to the first embodiment draws characteristic

impedance trajectory 7. When this capacitor is used, a resistance component of constituting components of the capacitor themselves (i.e., electrolytic solution 3, activated carbon 1b, power collection material 1a), which is known as so-called equivalent series resistance (ESR) 9, is increased. As a result, the impedance characteristic draws trajectory 8.

When the capacitor is further used, the equivalent series resistance is further increased to cause deteriorated material of electrolytic solution 3 to appear in electrolytic solution 3. Then, the deteriorated material is attached to the surface of activated carbon 1b and/or separator 2. Thereafter, resistance component to ion movement, which is known as so-called diffusion resistance component 10, is formed, thus causing the impedance characteristic to draw trajectory 11 having inflection point 12 caused by the deterioration of the electrolytic solution.

In view of the existence of inflection point 12, the present invention determines the deterioration by an impedance value within frequency region 13 that is lower than convex inflection point 12 at the upper side and that is higher than another convex inflection point 16 at the lower side. However, another inflection point 16 is inflection point 16 at which region 14 changes to region 13. At region 14, an impedance value rapidly changes from the frequency of 0(zero). At region 13, an impedance value gradually decreases. By doing this, the method for determining the deterioration of a capacitor according to the first embodiment can provide a result having a high accuracy that is substantially the same as that of the measurement result obtained from the DC voltage method and can

realize a power-saving measurement which is an advantage of the AC impedance method.

Fig. 4 is a flow diagram illustrating steps of the method for determining the deterioration of a capacitor according to the first  
5 embodiment of the present invention.

First, a deterioration characteristic of the same type of an electric double layer capacitor as that of capacitor 52 to be used is obtained. According to the first embodiment, a capacitor for which the deterioration characteristic is desired to be obtained is applied  
10 with a load (2.0V to 2.5V) at a temperature of 50 degrees C. After 10000 to 15000 hours, the impedance characteristic is measured. This deterioration characteristic also can be measured with a shorter time by further increasing the temperature.

Based on this impedance characteristic at which the  
15 deterioration is caused, inflection point 12 caused due to the deterioration of electrolytic solution is calculated. Then, a frequency lower than inflection point 12 is decided as a measurement frequency. This frequency and the impedance value are stored in deterioration measurement section 53. Based on the  
20 product design of a circuit including capacitor 52, a deterioration limit impedance value of capacitor 52 is determined and is stored in deterioration measurement section 53 (S1).

Then, when the circuit including capacitor 52 is operated, capacitor 52 gradually deteriorates. During the operation of the  
25 circuit, an AC voltage is applied to capacitor 52 whenever a predetermined time is reached, thereby measuring an impedance value with a predetermined frequency (S2).

Then, the measured impedance value is compared with the deterioration limit impedance value previously stored in the deterioration measurement section 53 (S3). When the measured impedance value is equal to or lower than the deterioration limit  
5 impedance value, then no abnormality is determined (S4: No) and capacitor 52 is continuously used. When the measured impedance value exceeds the deterioration limit impedance value on the other hand, capacitor 52 is determined as being deteriorated (S4: Yes) and abnormality display section 54 displays a request for the exchange of  
10 the capacitor by a warning light or the like (S5).

As described above, the method for determining the deterioration of a capacitor according to the first embodiment determines the deterioration of the capacitor based on an impedance value in frequency region 13 lower than inflection point 12 of the  
15 impedance characteristic. By doing this, the deterioration of the capacitor can be determined with a high accuracy, improving the determination reliability and saving the power used for the measurement.

When the deterioration of the capacitor is determined by  
20 measuring an impedance at a frequency higher than inflection point 12 of the AC impedance characteristic, the impedance value is low as shown in Fig. 3 even when the capacitor is deteriorated. Thus, the determination of the deterioration of the capacitor may include a significant error, causing a poor accuracy of the determination of the  
25 deterioration.

It is noted that Fig. 1 illustrates a basic circuit when electric double layer capacitor 52 is used according to the first embodiment

and the present invention is not limited to this circuit configuration.

(Second Embodiment)

In the method for determining the deterioration of a capacitor  
5 according to the second embodiment of the present invention, with  
regards to a capacitor deterioration limit characteristic, the DCR is  
firstly measured by the DC voltage method. Next, the method  
similar to that according to the first embodiment is used to measure a  
deterioration limit AC impedance characteristic (hereinafter referred  
10 to as  $Z$ ). Then, a correlation between the previously obtained DCR  
and  $Z$  is calculated. Fig. 5 illustrates the capacitor deterioration  
limit DCR/ $Z$  ratio according to the second embodiment of the  
present invention. In Fig. 5, the vertical axis and the horizontal  
axis are both logarithmic axes.

15 Based on Fig. 5, the DCR/ $Z$  ratio at a frequency lower than  
inflection point 15 at the capacitor deterioration limit is obtained and  
is stored in deterioration measurement section 53. Then, when the  
circuit including capacitor 52 is operated as in the case according to  
the first embodiment, capacitor 52 gradually deteriorates. During  
20 the operation of the circuit, an AC voltage is applied to the capacitor  
whenever a predetermined time is reached, thereby measuring  $Z$  at a  
predetermined frequency and measuring DCR. When the  
measured DCR/ $Z$  ratio is equal to or lower than the deterioration  
limit DCR/ $Z$  ratio previously stored in deterioration measurement  
25 section 53, the capacitor is determined as having no deterioration  
and is used continuously. When the measured DCR/ $Z$  ratio  
exceeds the deterioration limit DCR/ $Z$  ratio, then the capacitor is

determined as being deteriorated and the deterioration is displayed by a warning light or the like.

As described above, the method for determining the deterioration of a capacitor according to the second embodiment can  
5 increase the measurement accuracy of the AC impedance method, improving the reliability of the determination.

### (Third Embodiment)

The method for determining the deterioration of a capacitor  
10 according to the third embodiment of the present invention will be described with reference to Fig. 3. In Fig. 3, region 14 in which a capacitor impedance value rapidly increases from the frequency of 0(zero) is a capacitive frequency region representing a capacity component of a power gradient due to the self-discharge of the  
15 capacitor. Capacitive frequency region 14 can be used to determine the deterioration of the capacitor.

According to the third embodiment, the self-discharge can be used to suppress power consumed for determining the deterioration of the capacitor.

20 In order to increase the accuracy, an impedance value measurement using the AC impedance method or a capacity component measurement using the self-discharge of a capacitor in the present invention is desirably performed when the capacitor is not used and thus the voltage fluctuation is small.

25 Recently, this electric double layer capacitor has been suggested to be used as a power source for a vehicle such as a fuel cell vehicle. Power consumption by a power source is desired to be

suppressed as much as possible particularly in the case of an in-vehicle power source having a limited capacity. The impedance value measurement using the AC impedance method and the capacity component measurement by the capacitor self-discharge as  
5 described above are effective in the field as described above. In order to further improve the accuracy for determining the deterioration, the above measurement for an in-vehicle power source is also desirably performed when the capacitor is not used and thus the voltage fluctuation is small.

10 Although the third embodiment has described a case in which the capacitor is an electric double layer capacitor, the present invention is not limited to the third embodiment. The same effect also can be provided when the capacitor including a pair of electrode bodies having electrolytic solution therebetween is a redox capacitor.

15

#### INDUSTRIAL APPLICABILITY

The method for determining the deterioration of a capacitor in which electrolytic solution is provided between electrode bodies according to the present invention has an effect of saving power and  
20 is particularly useful when being used in a vehicle that is required to have a smaller size for example.

## CLAIMS

1. A method for determining deterioration of a capacitor including a pair of electrode bodies and electrolytic solution provided between  
5 the electrode bodies by applying an AC voltage to the capacitor to measure an impedance characteristic at a frequency of the AC voltage, comprising:  
previously calculating an inflection point appearing in the impedance characteristic due to the deterioration of the electrolytic  
10 solution to compare a characteristic value based on an impedance value in a frequency region lower than the inflection point with a predetermined characteristic value, thereby determining the deterioration.
- 15 2. The method for determining the deterioration of a capacitor according to Claim 1, wherein when the impedance characteristic is displayed such that a frequency value is higher while moving along a horizontal axis to the right and an impedance value is higher while moving along a vertical axis to the top, the inflection point is a first  
20 inflection point having a convex shape to the top and another inflection point different from the inflection point is a second inflection point having a convex shape to the bottom.
3. The method for determining the deterioration of a capacitor  
25 according to Claim 2, wherein the characteristic value is an impedance value at a frequency that is lower than the first inflection point and that is higher than the second inflection point.



4. The method for determining the deterioration of a capacitor according to Claim 2, wherein the characteristic value is a value that is calculated based on a correlation between an impedance value that  
5 is calculated by previously deteriorating the capacitor and a resistance value of a serial capacitor at a frequency lower than the first inflection point and higher than the second inflection point.

5. The method for determining the deterioration of a capacitor  
10 according to Claim 2, wherein the characteristic value is a capacity component obtained based on the voltage change due to the self-discharge of the capacitor at a frequency lower than the first inflection point and lower than the second inflection point.